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ORIGINAL PAPER

Wettability changes of wheat straw treated with chemicals and enzymes

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Abstract: A study was conducted to test wettability changes of the wheat straw treated with different methods for the preparation of wheat straw particle board. The wheat straws were separately sprayed with two chemicals (0.6% NaOH, 0.3% H_2O_2) and three enzymes (lipase, xylanase, cellulase). The contact angle between water and the surface of wheat straw was measured and the spreading-penetration parameters (*K*-values) were also calculated with wetting model. The surfaces of treated wheat straw and control sample were scanned by means of Micro-FTIR, and their peaks arrangements were analyzed. The surface morphologies of treated wheat straw and control sample were also observed by SEM. Chemical etching was found on the exterior surfaces of the straws treated separately with 0.6% NaOH and 0.3% H_2O_2; furthermore, the spreading-penetration parameters (*K*-values) of the distilled water on the exterior surfaces of the treated wheat straw along the grain were higher than that of control. The wettability of exterior surfaces of the wheat straws treated separately with lipase, xylanase and cellulose were improved after treating for seven days, and among the three enzymes treatments, the lipase treatment showed best result. The lipase treatment and NaOH treatment were determined as better methods for improving the wettability of wheat straw surfaces. However, in the economic aspect, NaOH treatment was more practical and easier in the pretreatment for the manufacture of straw particle board.

Keywords: wheat straw; wettability; contact angle; chemicals; enzyme

Introduction

Every year, about 8 hundred million tons of straws are produced in China. Straws are becoming the treasure of bio-mass which is rich in fibre and lignin. However, up to now, the straws have not been fully used and most of them are burned after harvest by farmers. Only a small quantity of straws was used in man-made straw panel due to the special surface properties of straw. The traditional adhesive such as urea-formaldehyde (UF) and phenol-formaldehyde (PF) are greatly restricted in manufacture of straw particleboard (Huang and Sun 2000). Diphenylmethane diisocyanate (MDI) had a better bonding but it is too expensive to be widely used. Therefore, using the traditional adhesives instead of the expensive MDI in the straw particle board becomes an attracting and a meaningful focus in the straw panel.

Wetting is an item to describe what happens when a drop of liquid place on the solid surface. The surface contact angle can reflect the wettability of solid material. The surface of wheat straw is quite different from wood. Many studies were carried out on the wetting on the surface of straw (Zhang and Hua. 2001, Wang et al. 2007, Liu et al. 2004, Pan et al. 2006, Wu and Zhou. 2003). The wettability has been used as an indicator of binding capability of an adhesive on fibers (Boquillon et al. 2004).

In the present study, wheat straw was separately treated with two chemicals and three enzymes, and the surface morphology of treated wheat straw was respectively characterized with SEM and Micro-FTIR, with an objective to provide technical support for preparation of wheat straw particle board.

Materials and methods

Materials

Wheat straw was obtained from the Mingshui Town, Heilongjiang Province, China. After harvest, the collected straws were dried in sunlight and then cut into small pieces, about 5 cm in length. The cut straws were air-dried for a few months in airy shelf to 7% moisture content. The 30% H_2O_2, purchased from chemical company, was diluted to 0.3% for use. The sodium hydroxide was analytical reagent. The cellulase, xylanase and lipase were purchased from Richeng enzyme Co., Ltd. Zhaodong City, Heilongjiang Province, China.

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Chemical and enzyme treatments

For control sample, distilled water was sprinkled on the surface of straw at the ratio of 3.5:1(water/straw). The 0.6% sodium hydroxide solution was sprinkled on the surface of straw at the ratio of 3.5:1(liquid/solid) for sodium hydroxide treatment, and 0.3% H_2O_2 solution was sprinkled on the surface of straw at the ratio of 3.5:1(liquid/solid) for hydrogen peroxide treatment (Liu et al, 2008) . Different kinds of enzyme were dissolved into citric acid-disodium hydrogen phosphate buffer solution for enzyme treatment. The pH value of buffer and dosage was 5, 99 IU/g, for cellulase; 5, 237 IU/g, for xylanase; and 7.5, 174 IU/g for lipase. The three enzyme solutions were separately sprinkled on the surface of straw. All the samples were put into oven and dried at 50ºC for a few days and then washed by distilled water. Finally, the samples were dried at 100−102ºC to approximately 4% moisture content for requirement of straw particleboard manufacture.

Contact angle measurement

A drop of water (2 μL) was placed on the surface of wheat straw using a 10-μL micro syringe, with three replicates, for wetting measurement. Wetting measurement of the specimens (2 mm × 15 mm in size) was performed at 17±2ºC using the JC2000C contact angle measuring Apparatus (CAA, made in Shanghai, P.R. China). The changing drop shape of water on the straw surface was captured and saved as a new file in computer every minute. As time elapses, the drop shape intended to stabilize (equilibrium contact angle was obtained). From initial contact angle to equilibrium contact angle couples data points were taken for each recorded drop to obtain a curve of contact angle vs. time. Three replicates were averaged for each sample. The drop on the surface of straw became smaller gradually due to water spreading and penetration.

Measurement of functional groups and surface morphology

The FTIR spectra of treated and untreated wheat straw (control) were obtained by using the 560-Fourier transform infrared spectroscopy (FTIR) (made in America, Nicolete Magna). Scanning electron microscope (SEM) images of the surface of control sample and treated wheat straw were observed by using the Quanta200 SEM (made in America, company FEI).

Determination of content of benzene-alcohol extractives

The content of benzene-alcohol extractives of wheat straw was measured according to the GB2677.2-81 of Chinese Standard.

Results and discussion

The K value measurement

Usually, contact angle indicates the wetting extent of liquid on solid surface. Three processes, initial contact angle, liquid drop spreading and liquid penetration, will happen step by step when the liquid drop is placed on the surface of straw. With the wetting model developed by Shi and Gardner (2001), the spreading and penetrating abilities of a liquid/solid system can be quantified. For an ideal liquid/solid system, the expression could be as Equation (1), which the contact angle (θ) changes as a function of time (t).

$$\theta = \frac{\theta_i \cdot \theta_e}{\theta_i + (\theta_e - \theta_i)\exp[K(\frac{\theta_e}{\theta_e - \theta_i})t]} \tag{1}$$

Where θ_i represents the instantaneous contact angle, θ_e represents the equilibrium contact angle, and K is the change rate constant of contact angle, and also K is the spreading/penetrating constant. The higher K value is, the quicker equilibrium is, and the better wettability is.

The K values of wheat straw treated with five different methods, calculated using Origin7.5, are shown in the Table 1.

Table 1 Contact angles and K values on different wheat straw surface

sample	θ_i (Degree)	θ_e (Degree)	Decrease percent (%)	K value(l/s) ($\times10^{-3}$)
Control	91	49	46.2	1.14
sodium hydroxide	84	15	82.1	3.57
hydrogen peroxide	88	26	70.4	2.32
cellulase treatment	88	18	79.5	2.23
xylanase treatment	87	11	87.4	3.24
lipase treatment	65	19	70.8	4.28

θ_i: instantaneous contact angle; θ_e: equilibrium contact angle.

As shown in the Table 1, the treated wheat straw had greater K value than the untreated (control sample). This attributes to the chemical changes between substance on surface of wheat straw and different chemicals or different enzymes, which could make the straw more hydrophilic. The lipase treated sample had the greatest K value (4.28×10^{-3}) and the initial contact angle was the smallest (65°) compared to other treatments,. Although the equilibrium contact angle of lipase treated sample was a little bigger than that of those treated with xylanase, cellulase, and sodium hydroxide, the K value overweigh the initial and the equilibrium contact angle in describing wettability according to Shi and Gardner's theory. Thus, lipase treatment also results in great change of wettability on wheat straw surface. Additionally, the initial contact angle of lipase treated samples is also the lowest among the five treatments. In view of manufacturing, the lower the initial contact angle is, the easier the bonding between straw and adhesives becomes.

Effect of treating methods on chemical groups on the surface of wheat straw

The FTIR spectrum of a–c in Fig.1 and a–d in Fig. 2 has a broad adsorption peak around 3 400·cm^{-1}. This strong peak was as-

signed to the stretching of the –OH group which is easy to be found in cellulose, lignin and aliphatic fraction of waxes. For Fig.1 curve c, the –OH group was more exposed resulted from the NaOH had partially defatted wax which covered on the wheat straw surface. Methyl, methylene and methine group vibrations appeared at 2 924·cm^{-1}(Sun et al 1995, Fang et al 2002, Moran et al 2008) and were present in all straw spectra. A small adsorption peak at 2 362·cm^{-1} was emerged in the FTIR spectrum of treated samples, and it was getting stronger and sharper after treating by chemicals and enzymes (Fig. 1, curves b,c and Fig.2, curves b, c, d). This peak was assigned to HN-CO-NH deformation vibration. The peaks at 1650, 1604, 1508, 1460, 1423, 1371 and 898·cm^{-1} are typically assigned to cellulose and lignin (Sun et al 1995). A strong adsorption peak at 1 051·cm^{-1} is assigned to C–O stretching in cellulose, hemicellulose and lignin (Sun et al 2004). The peaks for Si-O and O-Si-O stretching may occur at the region of 1300–1000·cm^{-1}(Wu and Zhou 2003, Yao et al 2003). Two medium intensity peaks, approximately at 1 258·cm^{-1}and 1 162·cm^{-1}, were found in this region of control sample (Fig. 1 curve a), but after treating by chemicals and lipase, the peak at 1 258·cm^{-1} was weaken, and the peak at 1162·cm^{-1} was almost disappeared (Fig. 1 curves b,c and Fig. 2 curve b). This observation indicates that chemical treatment could partially remove or destroy the stratum corneum and silicon layer that cover on the outer surface of wheat straw to protect the plant from environmental damage.

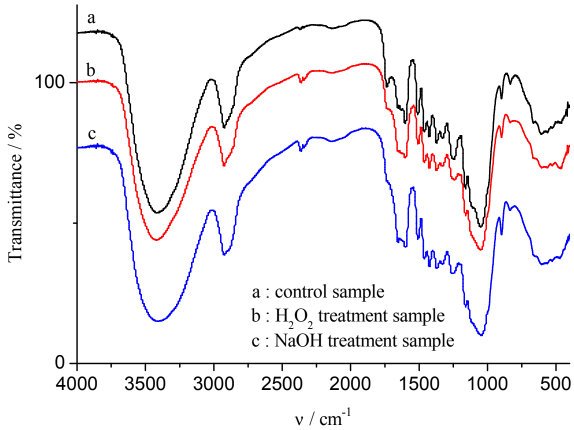

Fig.1 FTIR of chemical reagents treated straw

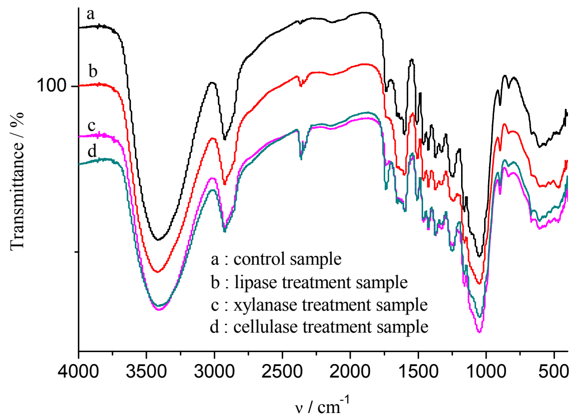

Fig.2 FTIR of enzyme treated straw

As observed previously by Hornsby et al. (1997), the outer surface was almost homogeneous, smooth, dense, and covered with a thicker waxy layer. The untreated wheat straw (control sample) showed a smooth surface and clearly displayed vascular bundles (Fig.3a). The NaOH treatment could effectively remove or destroy partial waxy substance and silicon layer as shown in Fig.3b. The effect of H_2O_2 treatment was not as obvious as NaOH treatment, but the pore on the wheat straw surface was more open (Fig.3c). The cellulase treatment and the xylanase treatment could not trip off the wax-like layer due to their specificity; they only destroyed the knot cell as showed in Fig.3d and e. For the lipase treatment, the stratum corneum on the outer surface was almost peeled off and a big pore was emerged. Fibre structure was exposed in the pore (Fig.3f). Anyway, the wettability of outer surface wheat straw was reduced because the wax and stratum corneum could be partially removed or destroyed by chemicals or enzymes to some extent. This phenomenon is called chemical or enzyme etching. In the process of particleboard making, the resin was easier to form the glue anchoring due to the coarse appearance and the exposed inner structure.

Zhang and Hua (2001) reported that the wax-like layer could weaken the bonding strength. The wax-like was consisted of lipophilic substance such as fatty acid and aliphalic alcohol, so the content of wax-like substance could be determined indirectly by measuring the content of benzene-alcohol extractives. In this experiment, the content of benzene-alcohol extractives of untreated straw (control sample) was 2.98%. The content of benzene-alcohol extractives was dropped to 1.79% after lipase treatment for one week and to 1.42% for two weeks, while the content of benzene-alcohol extractives of hydrogen peroxide treatment dropped to 2.14% for one week, 2.09% for two weeks and that of cellulase treatment dropped to 2.17% for one week, 1.99% for two weeks. The lipase treatment was definitely weakened the wax-like layer, and the wettability of exterior wheat straw was greatly improved.

Conclusions

By means of measuring the dynamic contact angle on the exterior surface of wheat straw, the spreading-penetration constant (*K* value) was used to quantify the wettability on the surface. The *K* values of treated samples were totally higher than that of untreated (control) sample. On the outer surface of treated wheat straw, the lipase treated samples had the highest *K* value (4.28×10^{-3}) and the lowest initial contact angle (65°) compared to other treatments, indicating that lipase treatment was the optimum method for improving the wettability of wheat straw among the three enzyme methods. The FTIR shows that the chemical groups on the outer surface of wheat straw had been changed a lot after treating by five different methods. It was considered that the cellulose and lignin was partially decomposed after treating with chemical reagents or enzyme. The characteristic absorption peak of SiO_2 in the FTIR imagines of

NaOH treatment or lipase treatment was sharply decreased. It implied that the O-Si-O structure was destroyed. The SEM images show that the stratum corneum was partially destroyed or removed on the treated straw exterior surface. The content of benzene-alcohol extractives was reduced to 1.79% (the control sample was 2.98%) after lipase treatment for one week. It is considered that the lipophilic substance composition of wax-like layer was degraded effectively. The lipase treatment and NaOH treatment are determined as better methods for improving the wettability of wheat straw. However, in the economic aspect, NaOH treatment was more practical and easier in the manufacture of straw particle board.

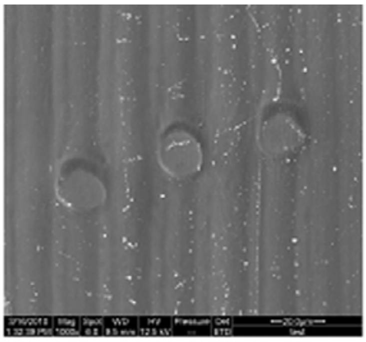

Fig.3a SEM of control sample

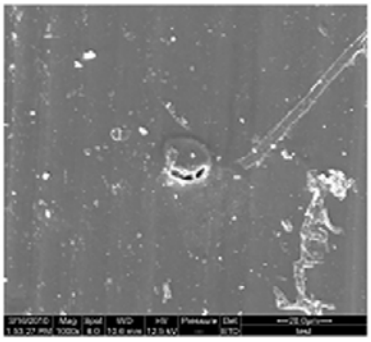

Fig.3b SEM of NaOH treatment sample

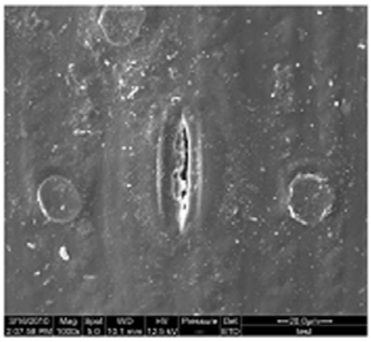

Fig.3c SEM of H2O2 treatment sample

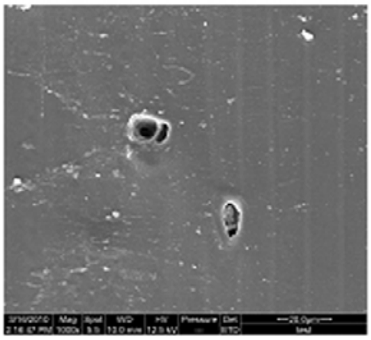

Fig.3d SEM of cellulase treatment sample

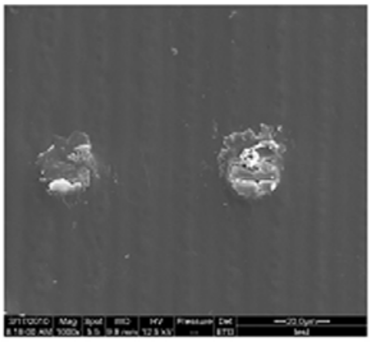

Fig.3e SEM of xylanase treatment sample

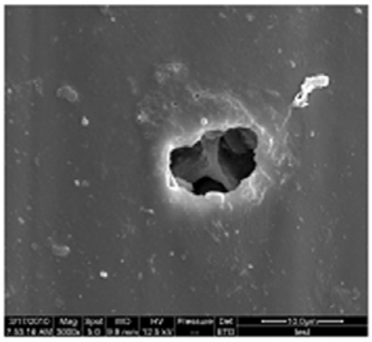

Fig.3f SEM of lipase treatment sample

Fig. 3 SEM imagines of all the samples

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